Universal linear-combination-of-atomic-orbitals parameters for d-state solids

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The assumption of a muffin-tin zero equal to the d-state energy, taken from Andersen's muffin-tin-orbital theory, is used in transition-metal pseudopotential theory to derive a simple form for the hybridization matrix element $\langle \vec{k}|\Delta|d \rangle$ in terms of a parameter r_d, given for all 27 transition elements. Using this form, matrix elements between d states on neighboring atoms are found to be given by $V_{ddm} = \eta_{ddm}\hbar^2 r_d^3/(md^5)$ with $\eta_{dd\sigma} = -45/\pi$, $\eta_{dd\pi} = 30/\pi$, and $\eta_{dd\delta} = -15/(2\pi)$. Thus for any structure and nearest-neighbor distance d, we need in addition only $\langle \vec{k}|W|\vec{k}\rangle$ (fitted to d-band energies calculated earlier) to provide all parameters needed for an elementary band calculation for any transition metal. Results are displayed for all. By replacing the free-electron band in this description by an sp band and equating appropriate band energies, we identify expressions for matrix elements coupling d states to s and p states. The universal form $V_{ldm} = \eta_{ldm}\hbar^2 r_d^{3/2}/(md^{7/2})$ is obtained but the coefficients obtained are sensitive to the matching procedure. Empirical values $\eta_{sd\sigma} = -3.11$, $\eta_{pd\sigma} = -2.82$, and $\eta_{pd\pi} = +1.35$ accord well with the bands given by Mattheiss for five cubic perovskites.

I. INTRODUCTION

In an earlier study[1] we extended pseudopotential theory to transition metals by extending the basis set in which the electronic states were expanded to include atomic d states as well as orthogonalized plane waves (OPW's). This led to a modified pseudopotential W which coupled plane-wave pseudowave functions and to a hybridization term Δ in the Hamiltonian which coupled the atomic d states and the plane waves. Both the pseudopotential and the hybridization were treated as perturbations. Moriarty[2] utilized a Green's function approach to improve the accuracy and has applied it to a number of properties.

Moriarty[3] subsequently showed that the tight-binding matrix elements between d states on neighboring atoms in transition metals could be written in terms of this hybridization, explaining the relation between these interatomic matrix elements and an intra-atomic resonance width noted earlier by Pettifor.[4] The origin of this relation is easily seen in terms of a perturbation-theoretic expansion in the hybridization, giving an indirect coupling

$$\langle d'|H|d\rangle = \sum_{\vec{k}} \frac{\langle d'|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|d\rangle}{E_d - E_k}. \tag{1}$$

The form of Moriarty's results for the interatomic matrix elements is also easily made understandable by writing $E_k = \hbar^2 k^2/2m$ and $E_d = \hbar^2 k_d^2/2m$. Then writing the sum over the wave number in Eq. (1) as an integral, one may continue the wave number into the complex plane, close the contour in the upper half plane, and pick up a residue from the poles at $k = \pm k_d$. A phase factor difference in the matrix elements in Eq. (1), equal to $e^{i\vec{r}\cdot\vec{d}}$

where $\vec{d}$ is the internuclear distance, leads to oscillatory terms in the interaction proportional to $e^{\pm i k_d d}$ as obtained by Moriarty.

In an alternative analysis of transition metals, Andersen[5] constructed a muffin-tin potential and noted that since the flat portion of the potential occupied so little volume in the metal the choice of the value of the potential in that region was quite arbitrary; its value had only a small effect on the resulting energy bands. He therefore took the simplest choice, a value equal to the energy of the d states. Using this potential he constructed muffin-tin orbitals, analogous to atomic states, and obtained matrix elements between them which varied with separation as d^{-5} and which had the simple ratios of $6:-4:1$ for $V_{dd\sigma}:V_{dd\pi}:V_{dd\delta}$,[6] the matrix elements with quantum numbers $m = 0$, 1, and 2. These results are in fact obtainable from Moriarty's[3] interatomic matrix elements by letting k_d approach zero, bringing the poles toward $\vec{k} = 0$. Andersen[5] made the same kind of construction for s bands and p bands, corresponding to a full linear-combination-of-atomic-orbitals (LCAO) treatment of the transition-metal bands.

Here we wish to use Andersen's choice of muffin-tin zero but return to the pseudopotential formulation so that the bands are treated as composed of LCAO d bands, hybridized with OPW's, as in many earlier interpolations of the bands[7] rather than with s and p states. Andersen's limit in fact enters in three different ways: First, it leads to a simple expression for the hybridization matrix elements in terms of a d-state radius r_d calculable from the atomic wave functions alone; second, it leads to interatomic matrix elements satisfying the relations given above, and written as simple functions of r_d; and third, it leads to an effective mass for

the free electrons, also a simple function of the single parameter r_d characterizing the atom.

II. FORM OF THE HYBRIDIZATION

If the atomic d states $|d\rangle$ were eigenstates of the Hamiltonian in the crystal, they would not be coupled to any other states nor to the OPW's in which we expand states. These d states are in fact eigenstates of the Hamiltonian in the free atom so that the matrix elements which do couple the d states to the OPW's arise from the difference between the Hamiltonian in the metal and that in the atom. Writing δV as the potential in the metal minus that in the atom, and writing the orthogonality of the OPW to the d states explicitly ($|\text{OPW}\rangle = |\vec{k}\rangle - \sum_{d'}|d'\rangle\langle d'|\vec{k}\rangle$; the orthogonality to other core states will not enter since we will see that δV is taken to be zero within the muffin-tin sphere where the core wave functions are nonzero), we obtain

$$\langle\text{OPW}|H|d\rangle = \langle\vec{k}|\delta V|d\rangle - \langle\vec{k}|d\rangle\langle d|\delta V|d\rangle. \quad (2)$$

d states on neighboring atoms, as well as other d states on the same atom, are taken as orthogonal to each other. It is convenient to define a hybridization potential Δ given by

$$\Delta = \delta V - \langle d|\delta V|d\rangle. \quad (3)$$

Then the coupling between an OPW and a d state is simply the matrix element of Δ between the corresponding plane pseudo-wave-function and the d state.

We may now make Andersen's assumption of a muffin-tin potential in the metal in order to obtain δV. It is equal to the atomic potential within the muffin-tin sphere radius r_{mt} but equal to ϵ_d outside. We choose r_{mt} such that the muffin-tin potential is continuous, as illustrated in Fig. 1. r_{mt} turns out to be somewhat smaller than the atomic sphere (or Wigner-Seitz sphere) radius so the view that $|d\rangle$ extends outside the muffin-tin sphere but does not overlap neighboring spheres or neighboring d states is consistent. Then δV is readily seen to be the cross-hatched region shown in Fig. 1. A remarkable feature of this assumption is that then the potential δV is determined entirely from the potential in the atom and is independent of the density of the metal, the atomic arrangement, or any screening. This is only an approximation to the potential, but it is a great simplification and we will see that it gives good results.

We may now proceed to the evaluation of the hybridization matrix element which enters Eq. (1). We take spherical coordinates with the z axis along the internuclear vector $\vec{d}$ from the atom containing the state $|d\rangle$ to that containing the state
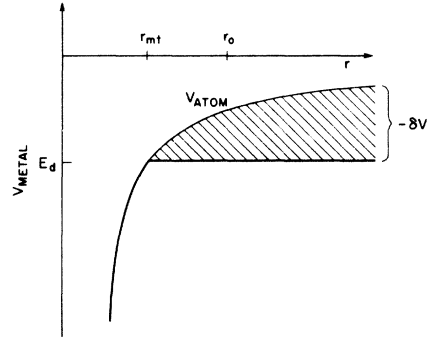

FIG. 1. The muffin-tin potential in a metal V_{metal} is defined to equal the free-atom potential V_{atom} within some sphere of radius r_{mt} and constant outside. In the Andersen form the constant portion is taken to equal the atomic d-state energy ϵ_d, and we choose r_{mt} such that the potential V_{metal} is continuous, as illustrated here. This r_{mt} turns out to be somewhat smaller than the radius r_0 of a sphere with volume equal to the volume per atom in the metal. The potential in the metal, minus that in the atom, then, is $\delta V = \epsilon_d - V_{\text{atom}}$ for $r \geq r_{mt}$, and zero for $r \leq r_{mt}$.

$|d'\rangle$. The angular coordinates measured with respect to this axis are written θ_1, ϕ_1, and the state is written

$$|d\rangle = R_2(r)Y_2^m(\theta_1,\phi_1). \quad (4)$$

R_2 is the radial d-state wave function and Y_2^m is the spherical harmonic. The plane wave may also be written in an expansion in spherical harmonics; let the axis for the corresponding coordinates θ_2,ϕ_2 lie along the vector $\vec{k}$. Then[8]

$$|\vec{k}\rangle = \frac{1}{\sqrt{\Omega}}\sum_l (2l+1)i^l j_l(kr)\left(\frac{4\pi}{2l+1}\right)^{1/2}$$
$$\times Y_l^0(\theta_2,\phi_2)e^{i\vec{k}\cdot\vec{r}_j}. \quad (5)$$

We have normalized the plane wave in the volume Ω of the system and $\vec{r}_j$ is the position of the atom in question. Since Δ is spherically symmetric around the nucleus only terms for $l = 2$ will enter $\langle\vec{k}|\Delta|d\rangle$. Furthermore, if we reexpand Eq. (4) in the coordinate system θ_2,ϕ_2, only the term with $m = 0$ with respect to $\vec{k}$ will contribute. That term is[9]

$$R_2(r)(\tfrac{4}{5}\pi)^{1/2}Y_2^m(\theta_k,\phi_k)Y_2^0(\theta_2,\phi_2), \quad (6)$$

where θ_k,ϕ_k give the orientation of $\vec{k}$ in the coordinate system θ_1,ϕ_1. Thus we may perform the angular integration to obtain

$$\langle\vec{k}|\Delta|d\rangle = \frac{-4\pi}{\sqrt{\Omega}}Y_2^m(\theta_k,\phi_k)e^{-i\vec{k}\cdot\vec{r}_j}\int_0^\infty j_2(kr)\Delta R_2(r)r^2dr. \quad (7)$$

We shall use this form for the hybridization matrix element in the band calculations.

If we take the d state to be well localized in comparison to the wavelength of the electron states of interest we may make the small-r expansion $j_2(kr) \sim k^2 r^2/15$. (We will discuss the validity of this at the end of this section.) Furthermore, we may write the volume of the system in terms of the atomic-sphere radius r_0 and the number N_a of atoms in the system, $\Omega = N_a \frac{4}{3}\pi r_0^3$ to obtain the convenient form:

$$\langle \vec{k} \,|\, \Delta \,|\, d \rangle = \left[\frac{\hbar^2 k^2}{N_a^{1/2} m}\right]\left[\frac{r_d}{r_0}\right]^{3/2} Y_2^m(\theta_k, \phi_k) e^{-i\vec{k}\cdot\vec{r}_j} , \quad (8)$$

with the d-state radius r_d defined by

$$r_d^{3/2} = -\frac{1}{5}(\frac{4}{3}\pi)^{1/2}\frac{m}{\hbar^2} \int_0^\infty r^4 R_2(r)\Delta dr . \quad (9)$$

(Note that R_2 has units of $r^{-3/2}$.) Its evaluation is straightforward and we carried it out for all $3d$ and $4d$ transition metals using Hartree-Fock d states R_2.[10] The results are in Table I.

It is interesting that by using the Schrödinger equation satisfied by $R_2(r)$ it is possible to write $\delta V R_2(r) = [\epsilon_d - V(r)]R_2(r)$ (for $r > r_{mt}$ and zero for $r < r_{mt}$) in terms of kinetic-energy terms and therefore to obtain r_d directly in terms of the atomic wave functions without using the potential itself. We used that method in obtaining the numbers in Table I. The results for r_d are also given in Table I, obtained[11] by fitting the bandwidths given by Andersen and Jepsen[12] using the atomic-sphere approximation.

We take the values fitted to the Andersen-Jepsen bandwidths to be correct r_d values. Then it is gratifying that the variation from element to element that we obtain from Eq. (9) is essentially correct, although our values are systematically too large. The difficulty appears to arise from our small-r expansion. We also evaluated Eq. (7) directly, as a function of k, without the small core expansion. At small k, of course, the expansion in small kr is valid but deviations become sizable

when k becomes as large as the wave number at a zone face. We will use the more accurate form Eq. (7) in calculating the energy bands, and in fact that is necessary to obtain good bands. That is not a significant computational problem but for formal purposes the simple k^2 form of Eq. (8) is preferable and it will be most meaningful if we use the fitted values of r_d from Table I. We shall use the simple form Eq. (8) in the following section.

In computing the bands of the $5d$ elements, we used the same $\langle \vec{k} \,|\, \Delta \,|\, d \rangle$ coupling as for the $4d$ series. This is justified since both r_d and the lattice parameters are very close in the two series. For V_{ddm} coupling we used the fitted r_d values from Table I in all cases.

III. INTERATOMIC MATRIX ELEMENTS

We may now evaluate the interatomic matrix elements Eq. (1) using Eq. (8). In pseudopotential theory Δ^2 is regarded as of the same order as the pseudopotential and since Eq. (1) is formally of order Δ^2, we may take the energy denominator as of zero order. With E_k measured from the muffin-tin zero at $E_d = \epsilon_d$, the denominator becomes simply $-\hbar^2 k^2/2m$ and the integration and the results are very simple, the second simplification resulting from Andersen's choice of muffin-tin zero. It might seem more natural to proceed as did Moriarty, writing the denominator as $\hbar^2(k_d^2 - k^2)/2m$. The message to be taken from Andersen's choice is that extra complexity arising from the poles at $k = \pm k_d$ is not essential to the problem and good results can still be obtained by letting k_d approach zero.

Taking this form for the denominator, taking spherical coordinates with axis along the internuclear distance, and substituting Eq. (8) into Eq. (1) gives

TABLE I. d-state radii r_d and d-band energies E_d for all transition elements.

3d	r_d (Å) Calc.[a]	r_d (Å) Fit[b]	E_d (eV)	4d	r_d (Å) Calc.[a]	r_d (Å) Fit[b]	E_d (eV)	5d	r_d (Å) Calc.[a]	r_d (Å) Fit[b]	E_d (eV)
Sc	1.80	1.24	7.10	Y	2.64	1.58	6.71	Lu		1.58	8.54
Ti	1.64	1.08	7.72	Zr	2.22	1.41	7.15	Hf		1.44	9.02
V	1.42	0.98	8.10	Nb	1.98	1.28	7.36	Ta		1.34	9.58
Cr	1.30	0.90	7.97	Mo	1.80	1.20	7.16	W		1.27	9.53
Mn	1.21	0.86	7.89	Tc	1.67	1.11	6.65	Re		1.20	8.98
Fe	1.15	0.80	7.68	Ru	1.58	1.05	5.98	Os		1.13	8.39
Co	1.09	0.76	7.38	Rh	1.49	0.99	5.04	Ir		1.08	7.35
Ni	1.03	0.71	6.90	Pd	1.41	0.94	4.54	Pt		1.04	6.54
Cu	0.98	0.67	5.90	Ag	1.35	0.89	2.46	Au		1.01	5.15

[a] Calculated from Eq. (9).
[b] Fitted (Ref. 11) to band widths given by Andersen and Jepsen (Ref. 12).

$$\langle d'|H|d\rangle = \frac{-8\pi r_d^3}{3\Omega}\frac{\hbar^2}{m}\sum_{\vec{k}}k^2 e^{i\vec{k}\cdot\vec{d}}Y_2^{m'}(\theta_k,\phi_k)^* Y_2^m(\theta_k,\phi_k)$$

$$= \frac{r_d^3\hbar^2}{3\pi^2 m}\int dk\,d\phi\,d\theta\,\sin\theta\,k^4 e^{ikd\,\cos\theta}Y_2^{m'}{}^* Y_2^m .$$

$$(10)$$

In the final form we have dropped the subscript k on the angular variables. The integration over ϕ gives zero unless $m'=m$, in which case it gives a factor of 2π. These matrix elements may then be written V_{ddm}, or (ddm) in the notation of Slater and Koster.[13] For each m we may substitute for the spherical harmonics and change variables to $x=-\cos\theta$ and $u=kd$ (giving a factor d^{-5} in front of the integral). The integral over k gives a series of terms of the form $u^n e^{iu}-(-u)^n e^{-iu}$ with varying powers of n. The remaining integrals over u may be written as a sum of integrals of $u^n e^{iu}$ along the entire real axis and the only contribution comes from the terms with $n=-1$. The evaluation of the numerical coefficient is somewhat tedious, although the form of the result

$$V_{ddm}=\langle d'|H|d\rangle = \eta_{ddm}\hbar^2 r_d^3/(md^5) \qquad (11)$$

follows immediately. The coefficients obtained are $\eta_{dd\sigma}=-45/\pi$, $\eta_{dd\pi}=30/\pi$, and $\eta_{dd\delta}=-15/2\pi$, having the same ratios as those obtained from muffin-tin-orbital theory,[6] or from taking the limit of Moriarty's forms.[3] Values are readily obtained using the fitted r_d from Table I.

We may note at this stage that corrections to the d^{-5} dependence of Eq. (11) would arise in going beyond the small-r expansion $j_2(kr)\sim k^2 r^2/15$. The addition of the next term, proportional to $k^4 r^4$, would add a term porportional to d^{-7} to Eq. (11); the next term would add a d^{-9}, etc. We proceed however, in the band calculation as well as in other calculations, keeping just the d^{-5} term, and only approximately account for the correction terms by using the fitted r_d.

IV. FREE-ELECTRON BANDS

In the transition-metal pseudopotential theory[1] the plane-wave states have energies:

$$E_k=\epsilon_d+\frac{\hbar^2 k^2}{2m}+\langle\vec{k}|W|\vec{k}\rangle$$

$$+\sum_d\frac{\langle\vec{k}|\Delta|d\rangle\langle d|\Delta|\vec{k}\rangle}{\hbar^2 k^2/2m} \qquad (12)$$

to first order in the pseudopotential. We have again made Andersen's choice in writing the zero-order energies as $\epsilon_d+\hbar^2 k^2/2m$. The final term vanishes at $k=0$ so the minimum of the band is at the energy $\epsilon_d+\langle 0|W|0\rangle$, which we write as an energy E_d below the d-band energy ϵ_d. The position of the free-electron minimum relative to the en-

ergy of the d bands is notoriously sensitive to the details of the potential in the metal, a problem which we have not addressed, and we shall take this position, the value of E_d, from the tables given by Andersen and Jepsen[11,12]; it is listed for each transition metal in Table I. The pseudopotential has a weak energy dependence, directly proportional to the orthogonalization hole,[14] but we take it to vanish, corresponding to a local pseudopotential.

The final term in Eq. (12), however, may be evaluated using Eq. (8). It gives the effect of coupling between the d states and the free-electron states and will be incorporated explicitly when we calculate the bands. However, it is interesting to evaluate it approximately using the perturbation-theoretical form of Eq. (12) to see how it has the effect of reducing the effective mass of the free-electron bands. Taking the axis of the polar coordinates along $\vec{k}$ only the state with $m=0$ contributes and with $Y_2^0(0,\phi)=(5/4\pi)^{1/2}$ it becomes $5\hbar^2 k^2 r_d^3/(2\pi r_0^3 m)$, corresponding to an effective mass of

$$m^*/m=[1+5r_d^3/(\pi r_0^3)]^{-1} \qquad (13)$$

and free-electron bands given by

$$E_k=\epsilon_d+\langle 0|W|0\rangle+\hbar^2 k^2/(2m^*) . \qquad (14)$$

This form can be useful in simple theories of transition metals where we do not explicitly include hybridization between the bands. The correction Eq. (13) incorporates one of the most important effects of hybridization. However, in calculating the bands, with explicit hybridization, we must use $m^*=m$.

V. ENERGY BANDS

We proceed next with the calculation of the bands. We construct a Bloch sum for each type of d state,

$$\chi_{d,m}=N_a^{-1/2}\sum_j|d,m\rangle_j e^{i\vec{k}\cdot\vec{r}_j} . \qquad (15)$$

The d^{-5} dependence of the V_{ddm} is sufficiently strong that we drop all but nearest-neighbor coupling, except for the body-centered-cubic structure where the second neighbors are only 15% more distant than the nearest neighbors. For that case we include both. For wave numbers along a cube edge (the z direction) in the cubic structures, the symmetry is sufficiently high that if we use the Koster-Slater forms[13] xy, x^2-y^2, etc., there are no matrix elements between Bloch sums of different d states, and we may directly compute the diagonal elements of the Hamiltonian matrix which become the band energies. The results are given in Table II. However, the Bloch sum for the d state of the

TABLE II. Diagonal Hamiltonian matrix elements for transition-metal bands. The free-electron band, Eq. (14) with $m^* = m$, is coupled to $E_{3z^2-r^2}$ by the matrix element in Eq. (7). All other off-diagonal elements (except $H_{xy,zx} = H_{yz,x^2-y^2}$ for hcp) vanish. All diagonal elements are measured from E_d.

bcc [001]. (A super (2) refers to second neighbors. a is cube edge.)

$$E_{xy} = (\tfrac{8}{3}V_{dd\sigma} + \tfrac{16}{9}V_{dd\pi} + \tfrac{32}{9}V_{dd\delta}) \cos(\tfrac{1}{2}ka) + 4V_{dd\pi}^{(2)} + 2V_{dd\delta}^{(2)} \cos ka$$

$$E_{yz} = E_{zx} = (\tfrac{8}{3}V_{dd\sigma} + \tfrac{16}{9}V_{dd\pi} + \tfrac{32}{9}V_{dd\delta}) \cos(\tfrac{1}{2}ka) + 2V_{dd\pi}^{(2)}(1 + \cos ka) + 2V_{dd\delta}^{(2)}$$

$$E_{x^2-y^2} = (\tfrac{16}{3}V_{dd\pi} + \tfrac{8}{3}V_{dd\delta}) \cos(\tfrac{1}{2}ka) + 3V_{dd\sigma}^{(2)} + V_{dd\delta}^{(2)}(1 + 2 \cos ka)$$

$$E_{3z^2-r^2} = (\tfrac{16}{3}V_{dd\pi} + \tfrac{8}{3}V_{dd\delta}) \cos(\tfrac{1}{2}ka) + V_{dd\sigma}^{(2)}(1 + 2 \cos ka) + 3V_{dd\delta}^{(2)}$$

fcc [001]

$$E_{xy} = 3V_{dd\sigma} + V_{dd\delta} + 4(V_{dd\pi} + V_{dd\delta}) \cos(\tfrac{1}{2}ka)$$

$$E_{yz} = E_{zx} = 2V_{dd\pi} + 2V_{dd\delta} + (3V_{dd\sigma} + 2V_{dd\pi} + 3V_{dd\delta}) \cos(\tfrac{1}{2}ka)$$

$$E_{x^2-y^2} = 4V_{dd\pi} + (\tfrac{3}{2}V_{dd\sigma} + 2V_{dd\pi} + \tfrac{9}{2}V_{dd\delta}) \cos(\tfrac{1}{2}ka)$$

$$E_{3z^2-r^2} = V_{dd\sigma} + 3V_{dd\delta} + \tfrac{1}{2}(V_{dd\sigma} + 12V_{dd\pi} + 3V_{dd\delta}) \cos(\tfrac{1}{2}ka)$$

hcp [c axis]

$$E_{xy} = E_{x^2-y^2} = \tfrac{9}{4}V_{dd\sigma} + 3V_{dd\pi} + \tfrac{3}{4}V_{dd\delta} + (\tfrac{1}{4}V_{dd\sigma} + \tfrac{5}{3}V_{dd\pi} + \tfrac{49}{12}V_{dd\delta}) \cos(\tfrac{1}{2}kc)$$

$$E_{yz} = E_{zx} = 3V_{dd\pi} + 3V_{dd\delta} - (2V_{dd\sigma} + \tfrac{7}{3}V_{dd\pi} + \tfrac{5}{3}V_{dd\delta}) \cos(\tfrac{1}{2}kc)$$

$$E_{3z^2-r^2} = \tfrac{3}{2}V_{dd\sigma} + \tfrac{9}{2}V_{dd\delta} + (\tfrac{3}{2}V_{dd\sigma} + 4V_{dd\pi} + \tfrac{1}{2}V_{dd\delta}) \cos(\tfrac{1}{2}kc)$$

$$H_{xy,zx} = H_{yz,x^2-y^2} = i\tfrac{1}{6}\sqrt{2}(3V_{dd\sigma} - 4V_{dd\pi} + V_{dd\delta}) \sin(\tfrac{1}{2}kc)$$

form $3z^2 - r^2$ is coupled to the plane wave $\vec{k}$ for $\vec{k}$ along the axis of the spheric coordinate system. The matrix element of that plane wave with the $m = 0$ state in Eq. (15) is evaluated using Eq. (8) to obtain

$$\langle \vec{k} | \Delta | \chi_{d,0} \rangle = \left(\frac{5}{4\pi}\right)^{1/2} \frac{\hbar^2 k^2}{m} \left(\frac{r_d}{r_0}\right)^{3/2}. \tag{16}$$

As we indicated earlier, this expression becomes inaccurate when k becomes large. We rectified this defect in the calculation of interatomic matrix elements V_{ddm} by using a smaller value of r_d. For the band calculation we evaluated Eq. (7) for $\langle \vec{k} | \Delta | d \rangle$ giving values which are nearly equal to the expression Eq. (16) but with our calculated r_d, and then drop below this, typically crossing zero at a wave number near the lattice wave number.

The energy bands then are given by the d bands of symmetry xy, $x^2 - y^2$, xz, and yz and two bands obtained from the coupled set by

$$E(k) = \tfrac{1}{2}[E_{3z^2-r^2}(k) + E_k]$$

$$\pm \{[\tfrac{1}{2}(E_{3z^2-r^2} - E_k)]^2 + H_{3z^2-r^2,k}^2\}^{1/2}. \tag{17}$$

The bands in the hexagonal-close-packed structure are complicated by the fact that there are two atoms per primitive cell, giving twice the number of bands. This difficulty is avoided by presenting

the bands in the Jones zone. Bloch sums with symmetries xy and zx are coupled, requiring solution of a quadratic equation. Bands from yz and $x^2 - y^2$ are identical; the two doubly degenerate bands are given in Table II. The $m = 0$ bands and free-electron bands require the addition of a second plane wave. The matrix element between the two is taken to be zero but this still requires solution of a cubic equation.

This completes an elementary band calculation for the three simple structures. The corresponding bands are displayed for all the transition metals in Fig. 2; manganese was taken in a body-centered-cubic structure rather than the true manganese structure and technetium was assumed hexagonal; for simplicity an ideal axial ratio was assumed for hcp structures.

VI. MATRIX ELEMENTS WITH s AND p STATES

For study of transition metals the mixed basis of plane waves and d states has been appropriate but in transition-metal compounds a full atomic-orbital basis is ordinarily preferable. In the same sense plane waves are most appropriate for the treatment of simple metals, but when these simple-metal atoms are part of a covalent or ionic structure an LCAO basis may be most convenient. In the covalent tetrahedral structures either basis
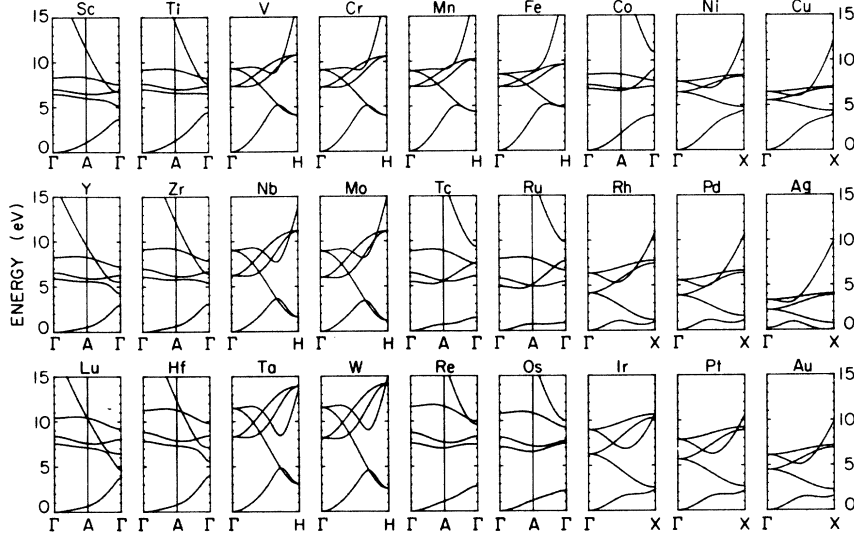
FIG. 2. The energy bands for all transition metals at the observed volume obtained from the formulas in Table II using the parameters given in Table I and the hybridization matrix element of Eq. (7).

can give a simple description of the bands. We recently recognized[15] that in fact if we assume that both the nearest-neighbor LCAO bands and the free-electron bands give the same band energies at points of highest symmetry in the Brillouin zone, we can deduce the corresponding interatomic matrix elements explicitly. This analysis leads to interatomic matrix elements among s and p states of the form $V_{ll'm} = \eta_{ll'm}\hbar^2/md^2$ with coefficients given for tetrahedral, simple-cubic, and body-centered-cubic structures in Table III. These matrix elements agree well with values derived earlier by empirical fits to the bands of tetrahedral semiconductors.[16] We may then seek matrix elements between d, s, and p states by making an analogous analysis of the transition-metal bands given here.

A natural way to do this is to relate free-electron states to s and p states as done in our analysis for semiconductors.[15] Then the matrix element with a d state, which will contain the $V_{sd\sigma}$, $V_{pd\sigma}$, and $V_{pd\pi}$, may be set equal to the expression for $\langle \vec{k} | \Delta | \chi_d \rangle$ given in Eq. (16). This will be shown to

TABLE III. Theoretical η coefficients for various structures.

	tet.	sc	bcc (nearest neighbor)
$\eta_{ss\sigma}$	−1.39	−1.23	−0.93
$\eta_{sp\sigma}$	1.79	1.90	1.75
$\eta_{pp\sigma}$	3.24	3.70	4.63
$\eta_{pp\pi}$	−0.93	−1.23	−0.93

give matrix elements of the form

$$V_{ldm} = \eta_{ldm}(\hbar^2/m)r_d^{3/2}/d^{7/2} .\qquad(18)$$

To obtain the coefficients we shall equate the lowest moment of k^2 in an expansion around $k = 0$. Although Eq. (16) was derived from atomic states and therefore is independent of the crystal structure, the values of the numerical coefficients η in Eq. (18) will depend on the structure. We will use the simple-cubic structure which seems more appropriate for the transition-metal compounds than the close-packed structures with their high coordination numbers.

Using forms for matrix elements from Slater and Koster[13] and explicit sp matrix elements from Ref. 15 the actual calculation is straightforward. With a k vector in the [110] direction the results are

$$\langle (s+p)_k | \Delta | xy \rangle = \tfrac{1}{2}(1 - 4/\pi^2)^{1/2}V_{pd\pi}k^2d^2$$

$$(19)$$

$$\langle (s+p)_k | \Delta | 3z^2 - r^2 \rangle = [\tfrac{1}{2}V_{sd\sigma} - \tfrac{1}{4}(1 - 4/\pi^2)^{1/2}V_{pd\sigma}]k^2d^2 .$$

These are equated to the corresponding expansions from Eq. (16) $[r_0^3 = (3/4\pi)d^3]$:

$$\langle k | \Delta | xy \rangle = \frac{1}{2}\sqrt{5}\,\frac{\hbar^2 k^2}{m}\left[\frac{r_d}{d}\right]^{3/2} ,$$

$$(20)$$

$$\langle k | \Delta | 3z^2 - r^2 \rangle = -\frac{1}{2}\left[\frac{5}{3}\right]^{1/2}\frac{\hbar^2 k^2}{m}\left[\frac{r_d}{d}\right]^{3/2} ,$$

to give the desired result Eq. (18). Muffin-tin-orbital theory[6] gives $V_{pd\sigma} = -3^{1/2}V_{pd\pi}$, and we can determine the numerical coefficients:

$$\eta_{sd\sigma} = -\tfrac{5}{2}(\tfrac{5}{3})^{1/2} = -3.23 ,$$

$$\eta_{pd\sigma} = -\sqrt{15}/(1 - 4/\pi^2)^{1/2} = -5.02 , \qquad (21)$$

$$\eta_{pd\pi} = \sqrt{5}/(1 - 4/\pi^2)^{1/2} = 2.90 .$$

The form Eq. (18) is independent of the structure we assumed and of the precise matching procedure (our use of the lowest moment in k^2), but the values of the coefficients depend sensitively upon both. For this reason we have confidence in Eq. (18), but not the values given in Eq. (21). In view of this uncertainty the best procedure seems to be to use the general form Eq. (18), and to derive empirical coefficients from known band structures. This will both test the form and give values to be compared with Eq. (21).

VII. BANDS IN TRANSITION-METAL COMPOUNDS

The analysis has given simple forms for all nearest-neighbor interatomic matrix elements needed for the construction of bands for any d-state compound. These could be used in an elementary LCAO band calculation for a compound of interest and indeed the bands in transition-metal compounds are frequently represented in this way. In particular, Mattheiss[17] has fit his carefully calculated energy bands for five perovskite compounds (obtained with the more accurate first-principles augmented-plane-wave (APW) method) by adjusting LCAO matrix elements. The most interesting comparison which can be made here is to equate our general form Eq. (18) for these matrix elements, using the r_d from Table I, to his values and deduce the coefficients η_{ldm} from each compound. If the coefficients prove independent of material, the form of Eq. (18) is confirmed, and we obtain empirical values for the coefficients. The results of this calculation are given in Table IV. The fact that each of the three coefficients

TABLE IV. Interatomic matrix elements for perovskites, obtained by Mattheiss [a] (adjusted where available) and the values of η_{ldm} which must be used in Eq. (18) to predict them. The degree to which each η_{ldm} is independent of material supports the theoretical formula Eq. (18).

a	KNiF₃	SrTiO₃	KMoO₃	KTaO₃	ReO₃
d (Å)	2.01	1.95	1.96	1.99	1.87
r_d (Å)	0.71	1.08	1.20	1.34	1.20
$V_{sd\sigma}$ (eV)	−1.15	−2.56	−2.99	−3.42	−3.53
$V_{pd\sigma}$ (eV)	−1.05	−2.25	−2.78	−3.06	−3.54
$V_{pd\pi}$ (eV)	0.51	1.14	1.25	1.39	1.62
$\eta_{sd\sigma}$	−2.89	−3.12	−3.15	−3.23	−3.15
$\eta_{pd\sigma}$	−2.64	−2.47	−2.92	−2.90	−3.17
$\eta_{pd\pi}$	1.29	1.38	1.32	1.32	1.45

[a] Reference 17.

obtained varies little from material to material, while the matrix elements themselves vary considerably indicates that in fact Eq. (18) reproduces rather well the trends from material to material.

We may take averages of the coefficients to obtain universal empirical values of

$$\eta_{sd\sigma} = -3.11 ,$$

$$\eta_{pd\sigma} = -2.82 , \qquad (22)$$

$$\eta_{pd\pi} = +1.35 .$$

These empirical coefficients do not agree well with the values −3.23, −5.02, and 2.90 obtained by fitting the first moments, nor with values we obtained from other plausible matching procedures. Note that the ratio of $V_{pd\sigma}/V_{pd\pi} = -2.08$ is not too far from the ratio −1.73 predicted by Andersen et al.[6] The only test of these matrix elements in other structures to date has been in the pure metals, requiring a very large extrapolation in terms of internuclear distance,[11] but comparison with the known bands indicated that these values [Eqs. (18) and (22)] are meaningful even there.

In using these matrix elements for other transition-metal compounds we need also the atomic term values (the diagonal matrix elements) for the solids. Our experience with the tetrahedral solids[10,15,16] has suggested that the term values for the free atom are a reasonable choice. If this is assumed also for d-state compounds (which appears appropriate at least for elements to the left of the transition series[10]) we would choose Hartree-Fock-term values[18] for the d states. Then the corresponding Hartree-Fock values can be used for the atomic states on the nonmetallic or nontransition atoms as well.

With such parameters the band calculation for any transition-metal compound is quite simple, generally simpler than in the transition metals themselves since the d bands ordinarily become separated in energy from the sp bands associated with the nonmetallic atoms. As with the transition metals themselves, we cannot expect the calculated bands to be as accurate as full sophisticated machine calculations with methods such as the APW method. On the other hand, they can be performed entirely in terms of the parameters given here, using only a hand-held calculator, for any compound for which the crystal structure is known. Furthermore, the description of the electronic structure is so simple that a considerable range of dielectric and bonding properties of the compounds can also be simply and directly calculated.[11]

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